Synthesis of Transition Metal Nitride Nanoparticles by Nitrogen DC Arc with Thermodynamic Consideration

H. Nogami, K. Yamashita, Y. Takemoto, M. Tanaka, and T. Watanabe

Department of Chemical Engineering, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

Abstract: Synthesis of metal nitride nanoparticles by DC arc has many advantages. However, the nitridation process has not been well understood. Nanoparticles of TiN and Cr_2N were successfully synthesized by nitrogen DC arc, while CeN nanoparticles were not formed. The formation of transition metal nitrides was controlled by their thermodynamic stability. Obtained remarks suggest that nitrogen DC arc is a promising tool to produce a large amount of transition metal nitride nanoparticles.

Keywords: thermal plasmas, functional nanomaterials, thermodynamic estimation

1. Introduction

Nanoparticles have unique properties that are different from those of bulk materials. For example, nanoparticles have a high chemical reactivity due to their larger specific surface area. In addition, depending on the type of materials, optical and magnetic features sometimes emerge. Because of such attractive features, nanoparticles have been studied in a wide range of fields such as catalyst and battery materials, miniaturization and performance improvement of electronic devices, and even in a medical field. They are expected to be practically used more and more in the future.

Metal nitrides are generally characterized by high hardness, high melting point, and high corrosion resistance. Some of them have useful functional properties such as high electrical conductivity and high thermal conductivity. Therefore, they have been applied to coating materials such as TiN, CrN, semiconductor materials such as GaN, AlN, and magnetic materials such as Fe_4N, $Fe_{16}N_2$. Further improvements of their characteristics can be expected by nanoparticulation of these metal nitrides. A lot of research on their properties and synthesis techniques are actively conducted in order to put them into practical use.

Thermal plasma has been utilized to synthesize nanoparticles for a long time because of high chemical reactivity and high enthalpy. Therefore, thermal plasma has the advantage of high production rate. The establishment of synthesis method for metal nitride nanoparticles by thermal plasma with these characteristics will become a significant contribution to the development of nanotechnology.

Although the synthesis of metal nitride nanoparticles by thermal plasma has been performed for a long time, the understanding of the nitridation process is insufficient. In this study, several metals are treated by DC arc in an Ar-N_2 atmosphere. Nitridation tendency are discussed based on thermodynamic considerations.

2. Experimental method

Figure 1 shows a schematic illustration of DC arc plasma system. This setup consists of a chamber, a collector, and DC power supply. Tungsten-2wt%La_2O_3 cathode was used. Cathode diameters was 6 mm. Water-cooled copper plate was set as the anode. Pure metals (Ti, Cr, Ce) were put on the anode as raw materials. Arc current was 100 A. Gas composition was 50vol%N_2-Ar at a pressure of 101.3 kPa. During the experiment, the gas was circulated by a circulation pump.

The synthesized nanoparticles were analysed through powders X-ray diffraction (XRD). The relative integrated intensity was calculated from the XRD results.

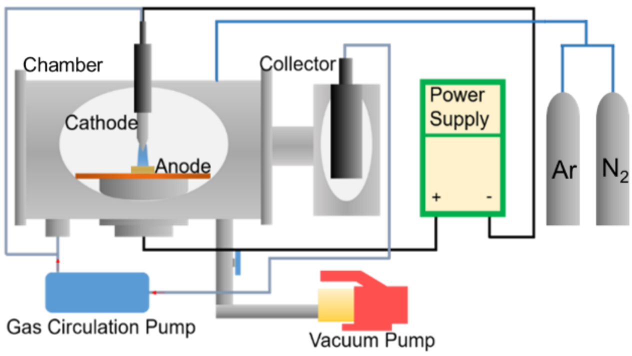

Fig. 1. Experimental setup of DC arc plasma.

3. Selection of raw materials

Raw materials were selected based on thermodynamic calculation by FactSage 8.1. **Figure 2** shows the Gibbs free energy change (ΔG) for the reaction between the metal and the N_2 molecule. Raw materials evaporate in the high-temperature area of the plasma, and nanoparticles are formed from the metal vapor through nucleation, condensation, and coagulation processes. Among these processes, nucleation and condensation are considered to be important processes that control the composition and crystallinity of nanoparticles and determine the characteristics of the final products.

Therefore, we focused on the ΔG value of the reaction with N_2 at nucleation temperature of nanoparticles. The nucleation temperature of nanoparticles is assumed to be the melting point of the nitride.

Figure 3 shows the ΔG values at the melting point of each metal nitride. Among these metals, Ti, Cr, and Ce were selected as raw materials to discuss the effect of ΔG value on nitriding.

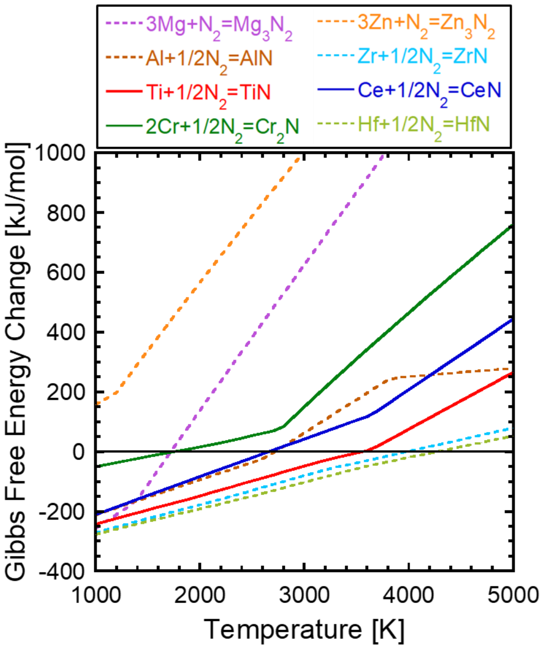

Fig. 2. ΔG of reaction between metals and N_2.

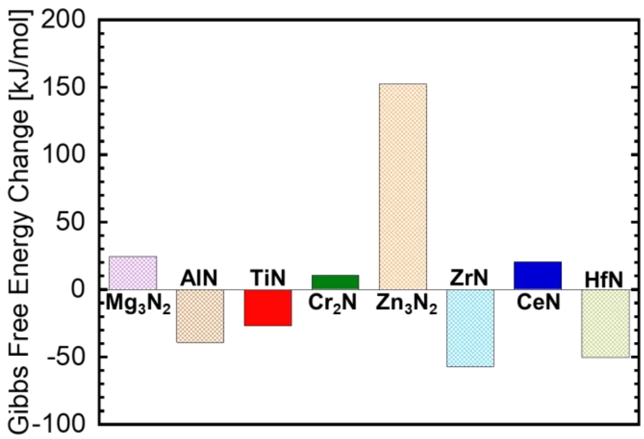

Fig. 3. ΔG at the melting point of nitrides.

4. Results and discussion

Figure 4 presents the XRD patterns of the synthesized nanoparticles. Titanium was completely nitrided to form TiN nanoparticles, while Cr and Cr_2N was synthesized in the case of Cr system. Cerium nitride nanoparticles were not formed but CeO_2 were confirmed. This is due to oxidation of as synthesized Ce nanoparticles by exposure to air in the process of gradually oxidation. Relative integrated intensity was calculated from the XRD peak areas. The relative integrated intensity of nitrides to products was unity for Ti, 0.45 for Cr, and 0 for Ce.

Figure 5 shows the relationship between the ΔG value at the melting point of the metal nitrides and the ratio of nitrides. The plots show a negative correlation. Obtained results clearly suggests that thermodynamic stability is most effective parameters to control the metal nitride formation.

5. Conclusion

Pure Ti, Cr, and Ce were treated by DC arc in Ar-N_2 atmosphere. The ratio of nitrides to products was estimated from the XRD results. The formation ratio of metal nitrides correlated with the thermodynamic stability of the metal nitride.

Acknowledgement

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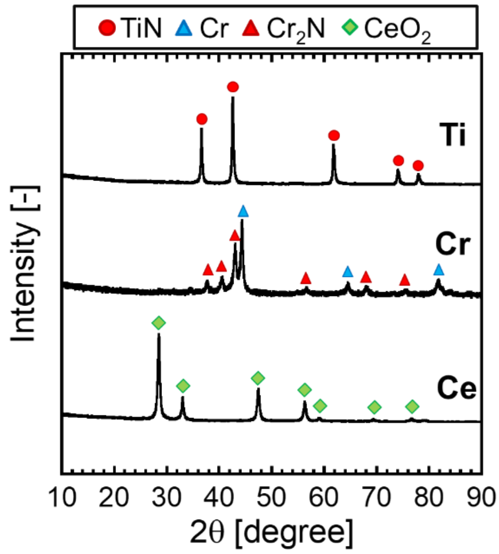

Fig. 4. XRD patterns of synthesized nanoparticles.

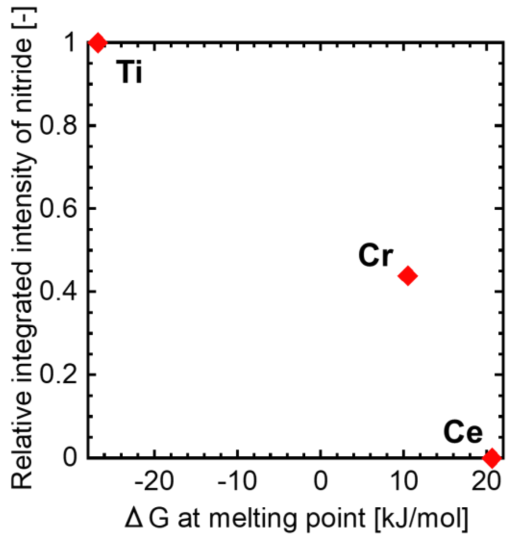

Fig. 5. Relationship between ΔG and relative XRD integrated intensity.